Polymer Bulletin 9, 125–131 (1983)

Polymer Bulletin

β Keto-Phosphonate Resins

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SUMMARY

The present paper describes two types of polymers with "hanging" β ketophosphonates groups. The first type was obtained by reacting carbanions of keto-phosphonates with chloromethylated polystyrene; the second one by reacting the same polymer with the tetramethylammonium salt of various β keto-phosphonates.

INTRODUCTION

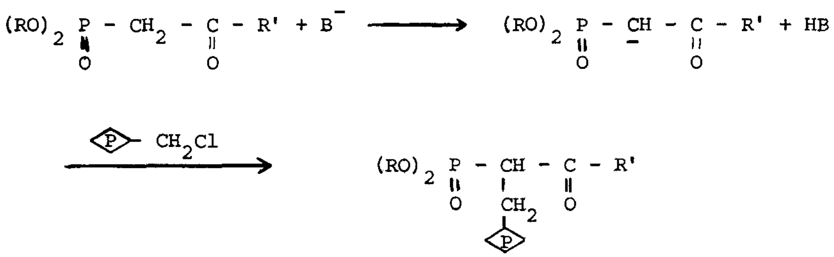
β keto-phosphonates give stable chelates with several metallic cations (1,2). This property was utilized in the study of the liquid-liquid extraction of couples of metals : Zn - Hf (3), Nb - Ta (4) and, more recently, U and Th (5). One of the disavantages of the liquid - liquid extraction is the use of large quantities of solvents. Therefore, it seemed interesting to have at our disposal polymerbonded chelatants, so that we could get resins with both the extracting properties of those keto-phosphonates and the advantages of such materials (handling, recovery...). Two principles of synthesis could be considered : creation of a polymerizable link on the ketophosphonate, followed by the polymerisation of the monomers thus obtained. This method meets with one difficulty, i.e. most of the phosphonate derivatives polymerize rather poorly, and high molecular weights are seldom reached (see (6) for examples). The second principle, which we found more interesting, consisted in directly grafting the keto-phosphonate on

0170-0839/83/0009/0125/$01.40

a leaving group bearing polymer. We chose chloromethylpolystyren, its chlorine of the benzylic type being a rather good leaving-group. The grafting technique consists in creating a nucleophilic center on the ketophosphonate, then to react it with the chlorinated polymer. Two means were used to create this nucleophilic center : either formation of a carbanion on the activated methylen group of the phosphonate, or formation of tetramethylammonium salt at one of its phosphonic ester functions.

Use of the carbanion of the ketophosphonate

The grafting principle may be schematized as follows.



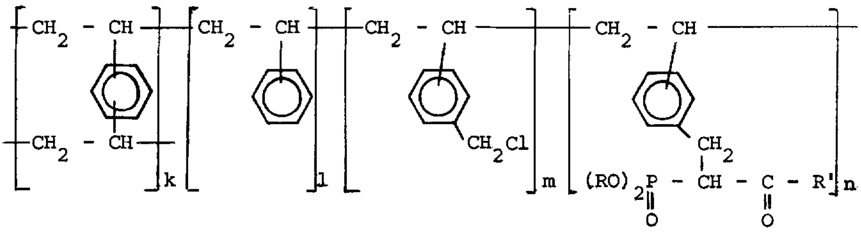
$$(RO)_2\underset{\underset{O}{\|}}{P} - CH_2 - \underset{\underset{O}{\|}}{C} - R' + B^- \longrightarrow (RO)_2\underset{\underset{O}{\|}}{P} - \underset{-}{CH} - \underset{\underset{O}{\|}}{C} - R' + HB$$

$$\xrightarrow{\text{Ⓟ}-CH_2Cl} (RO)_2\underset{\underset{O}{\|}}{P} - \underset{\underset{\text{Ⓟ}}{\underset{|}{CH_2}}}{\underset{|}{CH}} - \underset{\underset{O}{\|}}{C} - R'$$

$R = CH_3$, C_2H_5, nC_4H_9 ; $R' = C_nH_{2n+1}$; X ; C_nF_{2n+1}.

Ⓟ = Polystyrene.

The satisfactory course of this reaction greatly depends on the choice of the solvent, which must be a good solvent of the chloromethylpolystyren and, at the same time, compatible with the creation of the carbanion. The dimethylformamide (D.M.F.) gave the best result, while T.H.F. the weakest. The yield was calculated through elementary analysis of the remaining chlorine and checked through evaluation of the phosphonate remaining in solution. The polystyren not being 100 % chloromethylated, the "type I" polymers thus obtained may be schematized as follows :



- "Type I" resins -

Table I shows the results we obtained. The example of R' = phenyl (entries 7 to 10) establishes the superiority of D.M.F. as solvent (85 % yield) as opposed to only 3 % for T.H.F.. It seems this is primarily due to the poor solubility of the initial polymer, rather than the formation of the phosphonate carbanion, which can be equally achieved in both these solvents. The phase transfert catalysis, which gives good results in some cases of grafting (7), doesn't bring about any notable improvement in this case (entry 10).

From a structural point of view, a point was to be checked : make sure there was no O-alkylation. In this respect, the works of HEATHCOCK et al (8) may be referred to : the alkylation of oxo-2 propylphosphonates with benzyl bromide only leads to the mono C-alkylated derivative. The PCMS is likely to give the same result. Because of the light solubility of the resins in common solvents, (initial polymer cross-linked with 2 % D.V.B.), their N.M.R. spectra were poorly resolved. In order to cope with this difficulty, we made a few experiments with non cross-linked, more soluble, chloromethylpolystyren. In spite of this, we could observe a clear decrease of solubility of the phosphorylated resin, compared to the initial polymer . It is, however, possible to get workable data in the case of R' = phenyl. One may observe, on the one hand, the absence of ethylenic proton, thus verifying the exclusive C-alkylation and, on the other, the presence of a doublet at 3,48 and 3,86 ppm (1H) (J_{P-H} = 21 Hz), which is characteristic of the $\underset{\overset{\|}{O}}{P} - CH - \underset{\overset{\|}{O}}{C}$ proton. The integration isn't precise enough to observe whether or not there is some dialkylation (therefore reti-

Entry	R	R'	Solvent	% Cl	Yield	mm	n	m.eq. phosph. per g/resin
1	CH_3	pFC_6H_5	DMF	2,11	78	0,15	0,53	2,14
2	CH_3	CF_3	DMF	2,12	79	0,14	0,54	2,4
3	CH_3	C_7F_{15}	DMF	11,15	15	0,58	0,1	0,5
4	C_2H_5	CH_3	DMF	2,34	79	0,14	0,54	2,42
5	C_2H_5	nC_4H_9	DMF	2,7	73	0,18	0,50	2,1
6	C_2H_5	CF_3	DMF	7,45	41	0,4	0,28	1,3
7	C_2H_5	C_6H_5	DMF	1,35	85	0,1	0,58	2,19
8	C_2H_5	C_6H_5	THF	16,6	3	0,65	0,02	0,07
9	C_2H_5	C_6H_5	HMPT	2,82	72	0,18	0,42	1,8
10	C_2H_5	C_6H_5	NaOH P.T.C.(1)	6,66	55	0,30	0,37	1,42
11	C_2H_5	$pF.C_6H_5$	DMF	1,85	80	0,13	0,54	2,12
12	C_4H_9	CF_3	DMF	6,9	40	0,40	0,27	1,3
13	C_4H_9	C_6H_5	DMF	1,4	82,5	0,12	0,56	1,86

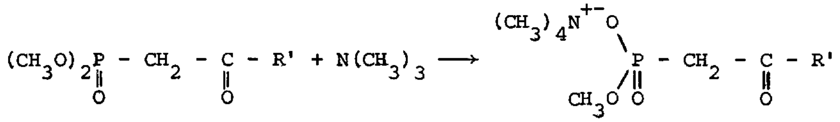
Table I :"Type I" resins
($k + \ell = 0,32$)

(1) Phase transfert catalysis

culation), but this could be the explanation for the poor solubility of the polymers obtained.

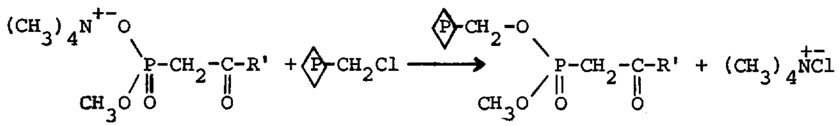
Use of the tetramethylammonium salt

One of the well-known properties of methylic esters of phosphoric acids is their ability to give tetramethylammonium (T.M.A.) salts when reacted with trimethylamine (9).When applied to various ketophosphonates, this reaction gives the corresponding T.M.A. salts, with very high yields.

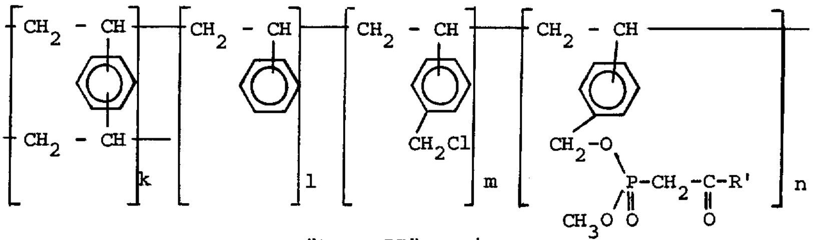


R$'$ = CH_3 ; C_6H_5, $pF-C_6H_5$, CF_3, C_7F_{15}

In the case of fluorinated phosphonates, the T.M.A. salts come out as thick oils that we were unable to cristallize. The salts thus obtained were reacted with P.C.M.S. according to the reaction :



As in the previous case, and for the same reasons, the yield depends on the solvent. It is optimal with D.M.F. The "Type II" resins obtained may be schematized as follows :



- "type II" resins -

Table II gives a few examples of resins obtained by this method.

Entry	R'	Solvent	% Cl found	Yield	m	n
1	CH_3	D.M.F.	0,14	96	0,03	0,65
2	C_6H_5	D.M.F.	0	100	0	0,68
3	p.F-C_6H_5	D.M.F.	1,26	86	0,1	0,58
4	p.F-C_6H_5	CH_3CN	4,7	57,5	0,29	0,39
5	C_7H_{17}	D.M.F.	0	100	0	0,68

Table II : "Type II" resins
$(k + \ell = 0{,}32)$

EXPERIMENTAL SECTION

The different β keto-phosphonates were prepared according to known methods (10, 11, 12, 13).

"Type I" resins. Typical procedure (Table I, entry 7).

0,5 g NaH (55 % in mineral oil) was washed several times with dry ether, then suspended in 100 ml dry D.M.F. Oxo-2 phenyl-2 ethyl phosphonate (2,56 g ; 10^{-2} mol) was added dropwise in order to keep temperature below 20°C (external cooling). A solution of 2g PCMS (FLUKA, 5 meq/g) in 90 ml DMF was then added. Stirring was continued 24 h at room temperature, then 2 h at 80°C. After cooling, the solution was poured into 600 ml dilute HCl, the resin filtered, washed with water and dried overnight in a vacuum oven at 80° C.

T.M.A. salt of β ketophosphonates. Typical procedure

To 7,1 g (0,12 mol) of $N(CH_3)_3$ in 30 ml dry acetone was added 16,6 g (0,1 mol) of dimethyl oxo-2 propyl phosphonate $(CH_3O)_2P(O)CH_2COCH_3$. The mixture was stirred and warmed 3 h at 80° C in a stainless steel bomb. After cooling, the TMA salt was filtered, washed with dry acetone, and dried over P_2O_5. We thus obtained 20,7 g (92 %) of $(CH_3)_4\overset{+}{N}\overset{-}{O}P(O)(OCH_3)CH_2COCH_3$.

"Type II" resins. Typical procedure (Table II, entry 1)

To a solution of 2 g PCMS in 90 ml D.M.F. was added 2,25 g of the preceeding salt. The mixture was warmed at 90°C with stirring for 2 h. After cooling, dilution with 600 ml water, filtration and drying (80° C), we obtained 2,5 g "Type II" resin.

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Received November 11, accepted November 21, 1982